Aerobic Mineralization of Paperboard Materials Used in Packaging Applications

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ABSTRACT: Aerobic mineralization of several different paperboard materials under laboratory-exposure conditions was studied. A novel respirometer was used to titrimetrically determine the kinetics of gas evolution and the rate of biodegradation was quantified by an empirical rate coefficient k. Various bleached paperboard materials studied showed about the same rate ($k = 0.14-0.16$ days^{-1}) and a 50–58 weight percent conversion of substrate carbon into carbon dioxide under the conditions used in the study. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1773–1779, 1999

Key words: aerobic mineralization; paperboard; lignocellulosic

INTRODUCTION

Paper is the predominant component of the municipal solid waste (MSW) stream as well as in urban litter; therefore, the question of the rate and extent of mineralization of paperboard is an important one. Paper and paperboard, being lignocellulosic materials, are well known to undergo biologically mediated degradation under suitable conditions.[1–3] In the case of bleached paperboard, which consists almost wholly of hollocellulose, the primary degradation products are saccharides that invariably mineralize into carbon dioxide and water. Biodegradability of any material, however, can only be assured in a biotic environment, and the lack of sufficient humidity and oxygen in typical sanitary landfills (where most of the MSW is disposed of)[4] to facilitate the biodegradation of paper, has been pointed out.[5] Even food materials contained in paper bags were observed to biodegrade very slowly in lysimeter exposure experiments.[6] In aerobic soil environments, however, the biodegradation of paper and most paperboard used in consumer packaging applications, apparently proceeds very well. However, the posttreatment of paperboard packaging materials, particularly the surface coating for water repellency (either with clay, wax, or polyethylene) and heavy printing could alter the biodegradability of the material.

A recent study on paperboard materials demonstrated the loss in mechanical integrity and the weight loss suffered by paperboard samples exposed to soil and laboratory biotic environments.[7] These changes that were observed in a time scale of about 10–12 weeks for a range of different samples do not necessarily indicate complete mineralization of the material. A moderate amount of biodegradation sufficient to weaken some of the fibers and the interfiber bonding is adequate to bring about the changes in bulk properties noted in the study. A complete biodegradation, however, requires the paperboard substrate to be totally converted into carbon dioxide, water, and biomass. The present study was undertaken to establish the timescale in which aerobic mineralization of paperboard samples (uncoated, wax-coated, and laminated) was obtained under laboratory conditions and to compare the results with the rate at which changes in bulk properties

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were obtained. A second objective was to study the effect of posttreatment of the paper by lamination or wax coating on the biodegradability. To ensure practical relevance of the data, actual consumer packaging materials were used in the study; these were the same materials used in a previous investigation.[7]

Biodegradation of Lignocellulosic Materials

Converting wood into paperboard involves pulping that mechanically breaks down the morphological structure of the wood tissue exposing more of the individual fibers. In the case of bleached paperboard, the pulp is delignified, usually chemically, to remove most, if not all, the lignin. Both of these conversion steps are expected to increase the biodegradability of the pulp. Removal of the recalcitrant lignin not only increases the readily biodegradable holocellulase content in the sample, but also breaks up the lignin-carbohydrate complexes, making the cellulose more easily accessible to enzymes and microbiota. Chemical[8] or biological[9] delignification of wood therefore generally leads to increased biodegradability. To impart water repellent properties, the paperboard used in packaging might be surface coated with wax or laminated with a plastic film. Printing either on the paperboard itself or more usually on the laminate is also done. The impact of these latter conversion steps on the biodegradability of the product is difficult to ascertain. Although it is reasonable to expect that the presence of a bioinert impermeable plastic laminate layer would seriously impair microbial access thereby discouraging biodegradation, our previous study[7] indicated quite the opposite. The presence of plastic layers trapped moisture in the paperboard, increasing the wet time available for biological activity. This effect apparently dominates, and in outdoor soil exposure experiments, the laminated paperboards biodegraded faster than the plain unlaminated samples.[7]

The mechanism of the biodegradation of cellulose, the principal component of bleached paperboard, is understood in terms of several enzymes acting in concert.[1,10] Endocellulases (1,4,β-D-glucan-4-glucanohydrolase) promote random hydrolysis of the macromolecular chain, resulting in a rapid drop in the average molecular weight of the polysaccharide. Exo-cellulase (1,4,β-D-glucan cellobiohydrolase) affects the endwise hydrolysis of the macromolecules at the nonreducing end yielding the disaccharide cellobiose. Cellobiases (β-D-glucoside glucohydrolases) occur widely in soil microorganisms and catalyze the hydrolysis of the 1,4,β-glycosidic links to yield glucose.[11] The sequential and cooperative activity of these three classes of enzymes results in the biodegradation of even highly crystalline cellulosic substrates.[12] Polysaccharides in the hemicellulose fraction of the pulp can be similarly biodegraded but may require additional enzyme systems such as glycanases for hydrolysis of heteroxylans.[13,14]

Lignin is also able to biodegrade, though at a relatively slower rate in the presence of appropriate microorganisms. Lignases, first isolated from *Phanerochaete chrysosporium,*[15] are present in many fungi including the white-rot fungi. It is a peroxidase that requires trace amounts of hydrogen peroxide for biooxidation.[16] Biodegradation by white-rot fungi generally takes place in the presence of a cosubstrate of carbohydrate or saccharides.[17] Other microorganisms, such as soil actinomycetes (for instance *Streptomyces badius*), however, can biodegrade milled-wood lignin even in minimal media.[18] Unlike holocellulose, the lignins do not always mineralize completely and the products of partial degradation are often incorporated into humic and fulvic acid components in the soil.

From an environmental standpoint, however, it is the complete mineralization that is of particular interest. This study therefore uses a respirometric method that quantifies the carbon dioxide evolved from the biodegradation process, to monitor the breakdown of paper substrates in biotic environments.

Assessment of Mineralization

The theoretical oxygen demand of cellulose and the maximum possible carbon dioxide yield on biooxidation of a carbohydrate are given by the following:

$$C_aH_bO_c + (2a + 0.5b - c)O = aCO_2 + 0.5H_2O$$

The CO_2 produced in biological oxidation of the compound, however, will be considerably less as some of the elemental carbon released by the substrate is incorporated into the biomass generated during the process. The microbiota that facilitate biodegradation use the energy as well as some of the carbon in the substrate for growth and reproduction. Yet, a substantial amount of the carbon in the substrate is also mineralized into CO_2.

Although measuring the amounts of CO_2 evolved per unit mass of biodegrading substrate is a useful measure of mineralization, it must be used with caution because of the partial conversion of the substrate carbon into biomass. Unfortunately, the yield coefficient, or the biomass yield per unit substrate loss during biodegradation, varies with the type of organic compounds used as a substrate as well as with inoculum characteristics. This precludes direct comparison of carbon dioxide evolution data from different experiments. When structurally similar substrates are used as in the present study on paperboard, and when the same inoculum is used with all samples, it is possible to obtain useful comparative data from mineralization experiments.

Several different types of respirometers have been described in the literature including the recent designs by Bartha[19] and by Andrady.[20] The latter is particularly suitable for the present experiments because it allows the frequent titrations to be performed in the biodegradation flask itself. Figure 1 shows the biometer flask used in the present study, with the upper section carrying the soil medium, inoculum, and the substrate. The flask contains a measured volume of dilute alkali to absorb any CO_2 liberated in the upper chamber. The two chambers are connected by a passageway through which denser CO_2 flows down into the flask. As with most designs, the biometer flask needs to be replenished with air periodically. This is done conveniently by removing the top half of the assembly (at the ground-glass joint) and replacing the flask with another containing a fresh volume of alkali. The removed flask is closed to prevent any pick up of atmospheric CO_2 and titrated against a dilute acid to determine the amount of CO_2 sorbed. The titrations need to be performed every 1 to 3 days to ensure that all oxygen in the biometer is not depleted. Usually, the biometer runs are conducted in duplicate, and a blank experiment as well as a reference substrate must be included in the test for comparative purposes. The net CO_2 evolution due to the substrate alone is obtained by subtracting the amounts liberated in the control biometer flask with no substrate (soil and inoculum only).

Typically, the test yields information on the rate of mineralization, the maximum mineralization achieved, and the lag-time. Data can be conveniently plotted in the form of a cumulative curve as shown in Figure 2 where the biodegradation of a low molecular weight cellulose (cellophane film) is compared with that of an intact lignocellulosic material (oak leaves).[20]

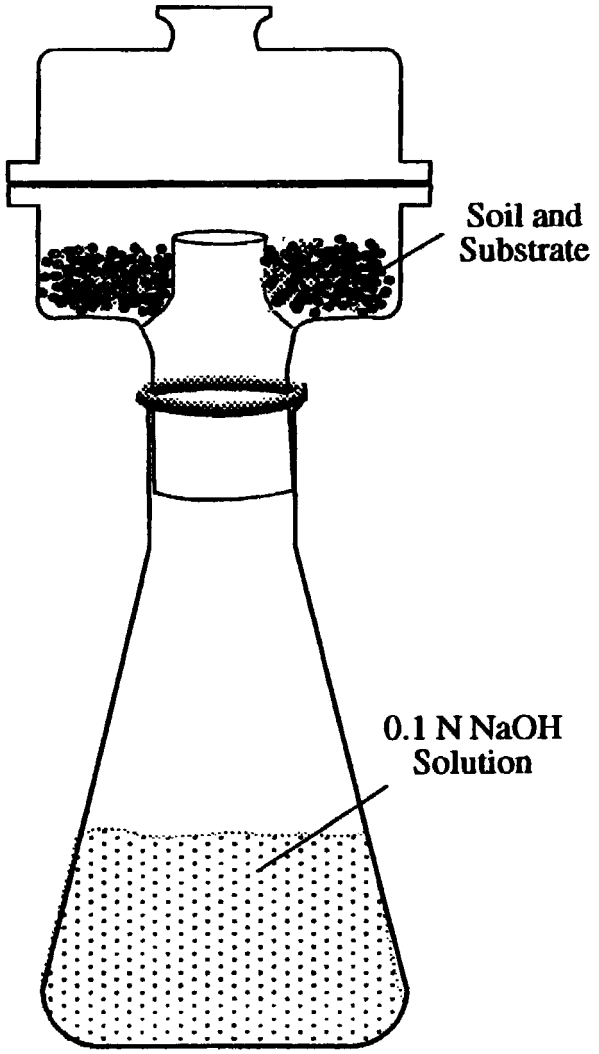

Figure 1 Schematic diagram of the novel respirometer for studying biodegradability of moderately biodegradable substrates.[20]

EXPERIMENTAL

All paperboard samples were obtained from various paperboard product manufacturers and the blotting paper reference material (manufactured by James River Inc.) was obtained from a commercial source. The samples were shredded in a laboratory grinder for about 1 min.

Mineralization

Approximately 70 g of moist, screened, never-fumigated topsoil (oven dry weight approximately

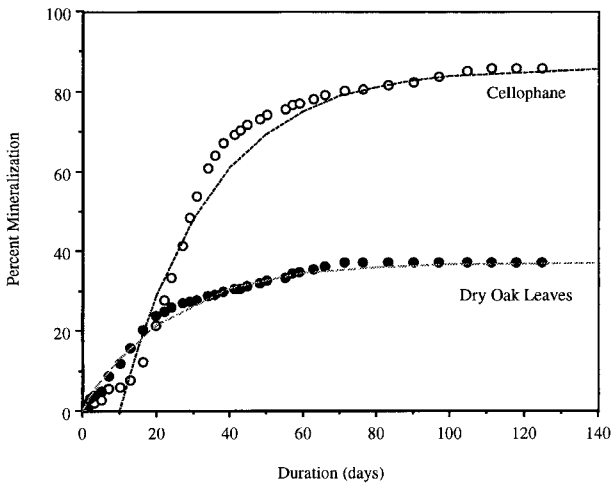

Figure 2 Mineralization data for a sample of uncoated cellophane film and fallen dried oak (*Querqus alba*) leaves

50 g) mixed thoroughly with 0.55 g of a 0.1% (w/w) solution of urea and 0.55 g of a 0.05% solution of potassium hydrogen phosphate, was used in each biometer flask. Aerobic sewage effluent containing 0.35 g/100 mL of suspended solids was used as the effluent. About 11 g of the effluent was added to the soil, intimately mixed with a glass rod, and the soil mixture was introduced into the biometer flask, and allowed to incubate at ambient temperature for 24 h. Accurately weighed samples (about 0.15 g) of the shredded paper samples were thoroughly mixed with the soil in the flask. An aliquot of 15 mL of 0.2*N* potassium hydroxide was placed in the flask and the ground-glass joint as well as the lid were sealed using a thin film of vacuum grease. The biometer assembly was incubated in the dark at ambient temperature. Duplicate flasks were used for each test material, the blotting paper reference, and for the soil blank with no substrate. Two biometers were used for each sample tested, for the blotting paper reference material, and for soil blanks. Once every 1 to 3 days, the bottom flask of each biometer was removed, the alkali reacted with about 2 mL of saturated barium chloride, and immediately titrated with 0.1*N* hydrochloric acid using phenolphthalein as an indicator. The flask that was removed was replaced by another that contained a fresh volume of the alkali. Preliminary experiments show that this switching of the flasks can be performed in ambient air without any significant errors being introduced into the procedure. In very accurate work with slowly-degradable materials, the switching of flasks need to be made in a glove bag flushed with CO_2 free air.

Klasson Lignin Determination

The procedure described in the standard method TAPPI T222 was followed.

Weight Fraction of Nonpaper Constituents

The fraction of plastic lamination on paperboard was determined by digesting a sample of known mass in 72% sulfuric acid followed by drying and weighing the indigestible plastic layer. The weight fraction of wax coatings was established by extracting a weighed sample of the paperboard with chloroform overnight followed by drying and reweighing.

Iodine Sorption

Iodine sorption was carried out according to the procedure described by Hessler and Power.[21] Essentially, a known mass of the shredded paperboard was reacted with iodine in potassium iodide. The excess iodine in the reaction mixture was determined titrimetrically using sodium thiosulfate. The milligrams of iodine adsorbed per gram of paper was calculated from the data.

RESULTS AND DISCUSSION

As seen in Figure 3, the mixing of paper substrate with the biotic soil medium did not immediately

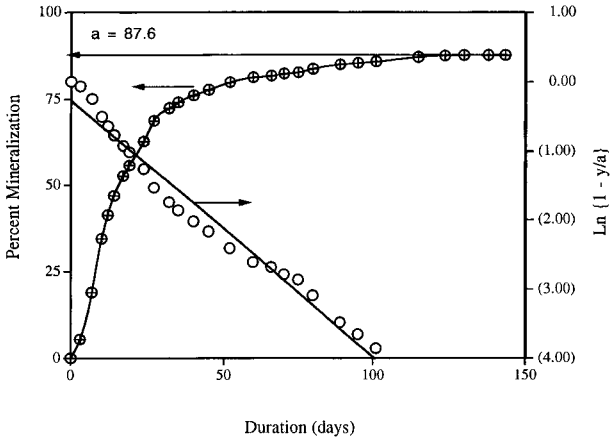

Figure 3 A sample plot of the gas evolution curve for a paperboard material incubated in soil inoculated with activated sewage sludge organisms. Also included is a plot of the same data as suggested by eq. (2), yielding a gradient k of 0.036 (days^{-1}).

Table I Mineralization Data for Different Paperboard Samples

Sample	Grammage[a] (g/sq m)	TCO_2[b]	ACO_2[c]	Percent of TCO_2	k ($days^{-1}$)	Percent Lignin	I_2 Absorption (mg/g pulp)	Coating Weight %
1. Blotting paper	260	0.153	0.884	57.9	0.176	0	119	0
2. Milk carton	510	0.142	0.070	49.7	0.157	4	107	7.67 (poly)
3. Frozen food carton	320	0.143	0.081	56.5	0.147	9	133	9.06 (poly)
4. Paper cup (hot beverage)	285	0.144	0.076	53.2	0.144	10	102	6.13 (wax)
5. Paper cup (cold beverage)	270	0.195	0.113	57.9	0.113	—	93	24.0 (wax)
6. Unbleached board	320	0.159	0.056	35.1	0.141	15	168	0

[a] Measured according to TAPPI T410-0m-88 standard procedure.
[b] TCO_2 is the theoretical amount (in grams) of carbon dioxide expected from the exact amount of substrate (usually 0.15 g) assuming all lignocellulosic material is mineralized. The weight of substrate was adjusted to take into account nonbiodegradable plastic laminate.
[c] ACO_2 is the actual amount (in grams) of carbon dioxide obtained from the mineralization of the sample.

result in the generation of measurable amounts of CO_2 gas, and a lag period of about 3 to 4 days was generally observed. The transfer of rapidly growing populations of microorganisms into new culture media (in this case paper substrate) can result in a lag phase in growth of organisms, because of the need to reconstruct the enzyme cell apparatus in response to the new medium.[22] However, the inoculum from sewage effluent is expected to be already adapted to paper substrate. Early stages of the biodegradation, possibly the hydrolysis of the polysaccharide into oligosaccharides, probably occurred during the lag time. Before such hydrolysis, biotic components need to establish intimate surface contact with the solid, insoluble substrate followed by the initial endergonic reaction.[23]

Thereafter, the evolution of gas was brisk and continued until the cumulative evolution curve in Figure 3 reached a plateau within a period of approximately 30 to 40 days. Most organic compounds that biodegrade in solution show this characteristic shape.[22,24] The carbon dioxide evolution curves for all samples of paperboard (including the unbleached sample) had the same general shape. Understandably, the lignin-containing unbleached paper sample displayed a smaller cumulative gas release compared with others. This is a reflection of the recalcitrance or at least the much slower rate of biodegradation of lignin relative to holocellulose. It is also seen in the data on oak leaves in Figure 1. To obtain an empirical rate coefficient for mineralization, it is convenient to plot the data as suggested by the following empirical relationship based on the shape of the curve:

$$y = a(1 - \exp(-k(t - c))) \quad (1)$$

where y is the fraction of substrate carbon that is mineralized at time t, c is the lag time to measurable gas evolution, a is the asymptote of the gas evolution curve, and k is the rate coefficient. To obtain values of y, the carbon content of the dry substrate was determined by elemental analysis. The values of k can be obtained graphically as the gradient of the following linear plot. Good estimates of lag time do not result from the same linear fit of the data but can be ascertained from the gas evolution curve. Note that $a = y_{max}$.

$$\mathrm{Ln}(1 - y/a) = -kt + kc \quad (2)$$

Plots for the present samples displayed a high degree of linearity ($r^2 = 0.98–0.99$) and very good reproducibility between the duplicate mineralization runs. The values of k derived from the plots are, however, dependent on the nature and the concentration of the inoculum used. Nevertheless, values relative to those for a reference substrate such as cellophane can provide a reliable measure of the rate of breakdown of the test substrate. Alternative measures of the kinetics of mineralization have been proposed. For instance, the milligrams of substrate carbon removed per milligram of dry inoculum solids per hour, has been proposed.[25] Although the kinetics of the increase in biomass has been used as an indirect measure of biodegradation,[26] it is of limited value because of the variation of the yield coefficient with substrates and the nature of inoculum.[27]

The rate coefficients listed in Table I show about the same degree of biodegradability for most samples ($k = 0.14$ to 0.18 $days^{-1}$). Because the paperboard substrates were finely shredded before testing, the effect of coatings and lamina-

tions in limiting microbial access by the lignocellulosic substrate will be minimal. Any differences should be related primarily to substrate composition. The observations on the unbleached board (sample 6) containing about 15% lignin (Klasson lignin determination) therefore suggests pulping to effectively break down the lignin carbohydrate complex to an extent that allows microbial access to the holocellulose. Sample 5, wax-coated paperboard, showed a significantly lower rate of breakdown of $k = 0.11$ days^{-1}. Apparently, the impregnation of the surface fibers of the board by liquid wax acting as a barrier was responsible for the slow down. However, the wax itself is biodegradable under these conditions at about the same rate as the paperboard (Andrady and Song, unpublished data from experiments in which wax samples were subjected to biodegradation using the same experimental method as described in this article). An important variable that could impact the rate of biodegradation of the paperboard sample is the fiber morphology, specifically the crystallinity of the material. Accessibility of the substrate morphology by enzymes can be approximated by experimental determination of Iodine absorption by the samples. The iodine uptake (milligram I_2 sorbed per gram of fiber) varied between 102 and 133 for bleached paperboard samples and yielded the low value of 93 for sample 5 which showed the slowest biodegradation.

The percent of carbon conversion, the value of parameter *a,* is often assumed to be a measure of the inherent biodegradability of the substrates. For most bleached pulps studied herein (see Table I), this percentage was 53 to 58 when corrected for the presence of nonbiodegradable polymer laminate in the composition. As might be expected, the unbleached paperboard sample (sample 6) yielded the much lower value of only 35%. A calculation assuming the lignin to be recalcitrant yields a conversion of 41% for this sample. In the case of soluble organic compounds, a 60% conversion rate over a 28-day period of incubation is typically expected of a readily biodegradable compound.[28]

The rate coefficients are, however, inoculum dependent and can only be used to relate the biodegradability of a sample to that of a reference material used in the same study. Furthermore, other significant sources of errors in mineralization estimates might be expected. For instance, the presence of a substrate, or its breakdown products in the biotic environment can result in retardation of the growth of biomass in the medium due to toxicity effects. Because the same effects are not obtained in the control biometer (with no pulp sample), an underestimation of the rate of mineralization is possible. Alternatively, where the breakdown products include nutrients such as monosaccharides (as with paper samples), they promote biomass growth that can biodegrade soil organic matter more effectively. This may result in an overestimation of the CO_2 evolution and hence biodegradability of the substrate.

It is tempting to assign a kinetic interpretation to the empirical relationship in eq. (2). This, however, is complicated by numerous limitations of the experimental technique used. The biodegradation occurs in a heterogenous system for which kinetic models are not readily available. Even assuming the substrate to be solubilized before degradation, the lack of information on the change in biomass and in substrate levels limits the application of most kinetic relationships derived for biodegradation of organic matter in aquatic systems.

In a previous study, we investigated the rate of loss in strength and in the weight of the same paperboard samples incubated in several soil environments (both inoculated and noninoculated). Unlike in the present study, however, the samples were exposed as large sheets (unshredded). This precludes a direct comparison of the rates of deterioration calculated in that study being directly compared with values of k (days^{-1}) in Table I. An important qualitative conclusion, however, is that in a time scale comparable to the loss in strength and weight of paperboard under biotic soil exposure, carbon dioxide evolution is also obtained. This suggests the physical deterioration observed in the large samples is to a large extent a result of true chemical breakdown of the lignocellulose substrate rather than to mere separation of the fibers in the paperboard.

CONCLUSIONS

Pulping and bleaching operations involved in the manufacture of bleached paperboard are likely to enhance the rate of aerobic mineralization of the material. All the bleached paperboard samples tested displayed approximately the same rate of breakdown and mineralized to a high enough extent to be classified as being readily biodegradable. The presence of a surface lamination or a wax coating did not impede the biodegradation of the shredded board samples.

The present data taken together with previously published data on the same paperboard samples suggest that the loss in integrity that accompanies biotic exposure of the paperboard is indeed accompanied by mineralization of the substrate.

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